

(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) EP 0 484 959 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
20.08.1997 Bulletin 1997/34

(51) Int Cl.: C08G 77/10, C08G 77/08,
C07F 7/08

(21) Application number: 91119057.7

(22) Date of filing: 08.11.1991

(54) Catalyzed redistribution of polyorganosiloxanes, and process for preparing cyclic siloxanes

Katalysierte Äquilibrierung von Polyorganosiloxanen und Verfahren zur Herstellung von
Cyclosiloxanen

Équilibrage catalysé de polyorganosiloxanes et procédé de préparation de cyclosiloxanes

(84) Designated Contracting States:
DE FR GB

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(43) Date of publication of application:
13.05.1992 Bulletin 1992/20

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Description

The instant invention is a catalyzed process for the redistribution of linear, chloride or hydroxy end-terminated polyorganosiloxanes or cyclic polyorganosiloxanes as defined below. In an additional embodiment of the instant invention, the catalyzed redistribution process is part of a three-stage process for producing high yields of cyclic polyorganosiloxanes as defined below. Effective catalysts for the described processes are alumina, silica-alumina, and zeolite.

Current industrial processes for the manufacture of silicone fluids, resins and rubbers typically require as starting materials either hydroxy end-terminated linear polyorganosiloxanes or cyclic polyorganosiloxanes. These polysiloxanes can be produced by the hydrolysis of lower molecular weight polyorganohalosiloxanes and diorganodihalosilane. This process results in a polydispersed mixture of cyclic and linear polyorganosiloxanes. Separation of this polydispersed mixture, to isolate a desired linear or cyclic fraction, results in an excess of either linear or cyclic materials, as well as materials of undesired molecular weight. Therefore, a process which allows for converting linears to cyclics and vice-versa and allows for adjustment of molecular weight of polyorganosiloxane chains is desirable to allow recovery of these excess siloxanes.

Known methods for enhancing the production of cyclic polyorganosiloxanes include cracking of the polyorganosiloxanes, which is capital intensive; vacuum hydrolysis, which has poor enhancement capabilities; and aqueous hydrolysis, which tends to sacrifice chloride recovery. Other methods for enhancing the production of cyclic polyorganosiloxanes require the addition of solvents or surfactants, which makes recovery of the product more difficult and can compromise product purity.

There are many reports in the patent literature dealing with redistribution of polyorganosiloxanes in the presence of halosilanes or a halogen substituted siloxane and a catalyst. See, for example, Sauer, U.S. Patent No. 2,421,653, Brown, U.S. Patent No. 3,065,252, Brown, U.S. Patent No. 3,101,361, Brown et al., U.S. Patent No. 3,162,662, Wegehaupt et al., U.S. Patent No. 3,549,680, Bennett, U.S. Patent No. 3,642,851, Bakassian et al., U.S. Patent No. 3,648,088, Frey et al., U.S. Patent No. 4,113,760,

US-A 4 113 760 (corresponding to FR-A 2 357 570) is concerned with a process for redistribution of cyclic polyorganosiloxane by the reaction of chlorosilanes with organosiloxanes. The reaction yields linear organosiloxanes.

EP-A 0 981 274 teaches a method for making cyclic polysiloxanes by feeding linear polyorganosiloxanes to a fixed catalyst bed to produce volatile cyclic polysiloxanes and by condensing and recovering the volatile cyclic polysiloxanes. The catalyst is an acidic catalyst, for example acid treated clay.

The present processes offer advantages over previously described processes. The present processes can be used not only to enhance the production of cyclic polyorganosiloxanes, but also to control the cyclic content from about zero to greater than 90 weight percent of the product. The described catalysts improve the rate of redistribution while minimizing organic cleavage. Cyclic polyorganosiloxanes as well as linear, chloride or hydroxy end-terminated polyorganosiloxanes can easily be redistributed to more desirable chloride-end terminated polyorganosiloxanes of 2 to 5 siloxane units. In addition, no solvents or surfactants are required and the catalyst are readily available and easily separated from polyorganosiloxane products.

The instant invention is a catalyzed process for the redistribution of linear, chloride or hydroxy end-terminated polyorganosiloxanes and cyclic polyorganosiloxanes. In a first embodiment of the instant invention, a polydispersed mixture of linear, chloride or hydroxy end-terminated polyorganosiloxanes is redistributed with an organochlorosilane or a linear, chloride end-terminated polyorganosiloxane of a lower degree of polymerization. In a second embodiment of the instant invention, the catalyzed redistribution process is part of a three-stage process which provides for controlled yields of cyclic polyorganosiloxanes. Effective catalysts for the described processes are alumina, silica-alumina, and zeolite and additionally activated carbon for the latter process.

Figure 1 of the drawing illustrates the three-stage process described herein. A column 3 is packed with a redistribution catalyst. The column 3 is connected to a reservoir 1 for feeding chlorosiloxanes to the column through a flow control device 2. Redistributed products from the column 3 are passed to a hydrolysis reactor 4, of a stirred-tank design, equipped with a stirring apparatus 5. Hydrogen chloride gas evolved in the hydrolysis reactor 4 is passed to a hydrogen chloride scrubber 6. Aqueous 36 weight percent hydrogen chloride is fed to the hydrolysis reactor 4 from a reservoir 8 through a metering device 9 and a hot oil bath 10, to provide make-up acid. The hot oil bath 10 heats the aqueous acid solution to compensate for heat lost from the evolution of hydrogen chloride gas. A portion of the reaction mixture is continuously withdrawn from the hydrolysis reactor 4 and passed to a phase separator 7. Within the phase separator, the hydrolysis mixture separates by gravity into an upper siloxane layer and a lower aqueous hydrogen chloride layer. The lower aqueous hydrogen chloride layer is withdrawn and recycled back to the hydrolysis reactor 4 along with aqueous make-up hydrogen chloride from reservoir 8 to maintain the interface level in the phase separator 7. The siloxane mixture is removed from the top of the phase separator 7 and passed to a flash distillation apparatus 11. The flash distillation apparatus is run under temperature and pressure conditions which cause cyclic polyorganosiloxanes and short-chain chloride end-terminated polyorganosiloxanes to be distilled out from higher molecular weight poly-

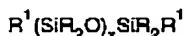
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ganosiloxanes. The higher molecular weight materials are withdrawn from the bottom of the flash distillation apparatus 11 and recycled through flow regulator 12 to column 3. The distilled cyclic polyorganosiloxanes and short-chain, chloride end-terminated polyorganosiloxanes are withdrawn through regulator 13, condensed in water cooled condenser 14 and collected in a suitable container.

5 In one embodiment, the present invention provides a process for the redistribution of chloride or hydroxyl-terminated polyorganosiloxanes, the process comprising:

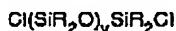
(A) contacting a first polydispersed mixture comprising siloxanes having the formula

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where each R is independently selected from a group consisting of hydrogen, alkyl and substituted alkyl radicals of one to six carbon atoms, R¹ is either Cl or OH, x is a mean value of 1 to 5,000, with a second mixture comprising chlorosilanes or chlorosiloxanes of the formula

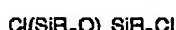


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where R is as previously described and y is a mean value of 0 to less than x in the presence of a catalyst which facilitates redistribution of chlorosiloxanes, the catalyst being selected from a group consisting of alumina, silica alumina, and zeolite for 1 to 60 minutes, and

(B) forming a redistributed mixture comprising chlorosiloxanes of the formula

25



where R is as previously described and z is a mean value greater than y and less than x if R¹ is Cl or less than x + 2y if R¹ is OH.

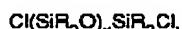
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Thus, in a first embodiment of the instant process comprises:

(A) contacting a first polydispersed mixture comprising either

35

(1) chlorosiloxanes of the formula



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(2) hydroxysiloxanes of the formula



45

or

(3) mixtures thereof;

where each R is independently selected from a group consisting of hydrogen and alkyl and substituted alkyl radicals of 1 to 6 carbon atoms, and x is a mean value of 1 to 5000; with a second mixture in the presence of a catalyst; and

(B) forming a redistributed chlorosiloxane mixture as defined above.

R is selected from a group consisting of hydrogen atoms and alkyl and substituted alkyl radicals of 1 to 6 carbon atoms. The alkyl radical can be, for example, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, sec-butyl, pentyl or hexyl. Preferred is when each R is independently selected from the group consisting of hydrogen atoms and methyl. Most preferred is when R is methyl. The substituted alkyl radicals can be of the general formula C_nH_{2n+1-a}X_a, where n is an integer from one to six, the value a is an integer from 1 to 2n+1 and x is a halogen.

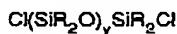
The preferred halogen is fluorine. The substituted alkyl radical can be, for example, 3,3,3-trifluoropropyl. When the substituted alkyl radical is 3,3,3-trifluoropropyl, it is preferred that R be independently selected from the group consisting of 3,3,3-trifluoropropyl and methyl.

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Preferred is where the chlorosiloxanes and hydroxysiloxanes have an average value for x in the range of 7 to 1000. Preferred is when all the R radicals are methyl.

The first polydispersed mixture of siloxanes can be formed, for example, by hydrolysis of diorganodichlorosilane. The second mixture comprises chlorosilanes, chlorosiloxanes or a mixture thereof of the formula:

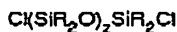
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where R is as previously described, y is a mean value of zero to less than x . Where the first mixture comprises a combination of chlorosiloxanes and hydroxysiloxanes or any combination thereof, an average value for the number of siloxane units in all siloxanes present, A_y , can be determined and y chosen to fall in a range from 0 to less than A_y . The preferred value for y is zero. Preferred is where the second mixture comprises chlorosilanes and chlorosiloxanes on which all R radicals are methyl.

The redistributed mixture comprises chlorosiloxanes of the formula

15



where R is as previously described; z is a mean value greater than y and less than x , when the first mixture is chlorosiloxanes; z is a mean value greater than y and less than $x+2y$ when the first mixture is hydroxysiloxanes; and z is a mean value greater than y and less than A_y' , when the first mixture comprises a combination of chlorosiloxanes and hydroxysiloxanes or any combination thereof. The value A_y' is a mean value equal to A_y plus the mole fraction of the hydroxysiloxane times 2y.

The first polydispersed mixture and the second mixture are contacted in the presence of a catalyst.

The catalyst which facilitates redistribution is selected from a group consisting of alumina, silica alumina, and zeolite. Silica-alumina refers to an amorphous compound containing both silicon oxides and aluminum oxides. In general, the more silicon dioxide present the lower the catalytic activity of the silica-alumina. Preferred, is when the silica is less than about 30 weight percent of the silica alumina compound. The term "zeolite" refers to crystalline aluminosilicates of Group IA and Group IIA elements such as sodium, potassium, magnesium and calcium. The zeolites effective in the process of the instant invention can be both synthetic and natural occurring zeolites, for example, as described in the Concise Encyclopedia of Chemical Technology. John Wiley and Sons, NY, 1985, pp. 772-774. A preferred zeolite is zeolite Y.

It is preferred that the catalyst be free of water prior to contact with the chlorosiloxane. Water can be removed from the catalyst by, for example, a vacuum, heating, treating with gaseous hydrogen chloride or treating with a chlorosilane.

The preferred catalyst is alumina. The first and second mixtures may be combined and then fed to a reactor containing the catalyst or may be individually fed to a reactor containing the catalyst.

Contact of the catalyst with the chlorosiloxanes can be effected by standard means for contacting liquids with solids, for example, a batch process or a continuous-flow process. The process can be conducted, for example, in a fixed-bed, a stirred-bed or a fluid-bed reactor.

The required contact time for the chlorosiloxanes with the catalyst, to effect redistribution, will depend upon such factors as temperature, type of chlorosiloxanes and type of catalyst. In general, contact times between about one to 60 minutes have been found useful. Longer contact times may be employed, however, undesirable levels of organic cleavage from silicon may occur. Shorter contact times may result in inadequate redistribution of the chlorosiloxanes. A preferred contact time is about five to 15 minutes.

The process can be run at a temperature between about 0°C. and 200°C. Higher temperatures may be run, but these can result in unacceptable levels of organic cleavage from silicon atoms. A preferred temperature range is about 25°C. to 60°C.

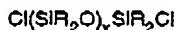
A preferred contact method is a continuous flow fixed-bed reactor. The volume ratio of the second mixture to the first mixture can be varied to affect the value z of the redistributed chlorosilane mixture. As the ratio increases z approaches y . A preferred range for this ratio is about 0.1 to 30.

The described process forms a redistributed mixture comprising chlorosiloxanes of the general formula $\text{Cl}(\text{SiR}_2\text{O})_z\text{SiR}_2\text{Cl}$, as previously described, with a mean value for the number of siloxane units of z . The value z is greater than y and less than x , $x+2y$, or A_y' , depending upon the composition of the first mixture.

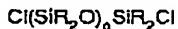
A second embodiment of the instant invention is a three-stage process for preparing cyclic siloxanes, the process comprising:

(A) contacting a first mixture comprising chlorosiloxanes of the formula

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5 where each R is independently selected from a group consisting of hydrogen atoms and alkyl and substituted alkyl radicals of one to six carbon atoms and x is a mean value of one to 5000; with a second mixture comprising chlorosilanes and chlorosiloxanes of the formula



10 where R is as previously described and p is a mean value of zero to 7; in the presence of a catalyst which facilitates redistribution of chlorosiloxanes selected from a group consisting of alumina, silica alumina, zeolite, and activated carbon;

(B) forming a redistributed mixture comprising chlorosiloxanes of the formula



20 where R is as previously described and q is a mean value within a range of greater than zero and less than seven;

(C) hydrolyzing the redistributed mixture of chlorosiloxanes to form a hydrolysate comprising cyclic siloxanes of the formula



25 where R is as previously described and g is a mean value of three to 25 and chlorosiloxanes;

(D) separating the cyclic siloxanes from the chlorosiloxanes; and

(E) recycling the chlorosiloxanes as a feed to step (A).

30 A method for conducting this three-stage process is represented schematically in Figure 1.

The process comprises contacting a first mixture comprising chlorosiloxanes of formula $\text{Cl}(\text{SiR}_2\text{O})_x\text{SiR}_2\text{Cl}$ and hydroxysiloxanes of the formula $\text{HO}(\text{SiR}_2\text{O})_y\text{SiR}_2\text{OH}$, or any mixture thereof; as previously described, with a second mixture comprising chlorosilanes and chlorosiloxanes of formula

35 $\text{Cl}(\text{SiR}_2\text{O})_p\text{SiR}_2\text{Cl}$, where R is as previously described and p is an average value within a range of 0 to 7, in the presence of a catalyst which facilitates redistribution of chlorosiloxanes, selected from a group consisting of alumina, silica alumina, zeolite and activated carbon. The latter catalyst can be carbon activated by treatment with anhydrous acid or chlorosilane. The catalytic activity of the activated carbon can be improved by bubbling gaseous hydrogen chloride through the carbon bed while conducting the redistribution processes described herein.

A preferred value for x in the three-stage process is in the range of one to 100.

40 A redistributed mixture comprising chlorosiloxanes of the formula $\text{Cl}(\text{SiR}_2\text{O})_q\text{SiR}_2\text{Cl}$ is formed, where R is as previously described and q is an average value within the range of 0 to 7. The catalysts, process temperature and contact times are as previously described. The method of contacting the first and second mixtures and the catalyst are as previously described.

45 The redistributed mixture of chlorosiloxanes is fed to a hydrolysis process where a hydrolysate is formed comprising cyclic siloxanes of the formula $(\text{R}_2\text{SiO})_g$, where g is an average value in a range of 3 to 25, chlorosiloxanes of the formula $\text{Cl}(\text{SiR}_2\text{O})_m\text{SiR}_2\text{Cl}$ and hydroxysiloxanes of the formula $\text{HO}(\text{SiR}_2\text{O})_n\text{SiR}_2\text{OH}$, as previously described. The hydrolysis reaction is run in the presence of stoichiometric or excess water in relation to the moles of chloride in the chlorosiloxanes to be redistributed. In general, the amount of excess water will be dictated by the method of chloride recovery, whether anhydrous or aqueous. The hydrolysis reaction can be run by standard methods, for example, in a continuous stirred tank reactor (CSTR), plug-flow reactor, fixed-bed reactor or a fluidized-bed reactor.

In the third stage of the instant process, the cyclic siloxanes are separated from the chlorosiloxanes and hydroxysiloxanes. This separation can be effected by first causing a phase separation of the hydrolysate into an aqueous hydrogen chloride phase and a siloxane phase. Phase separation may be accomplished by gravitational methods such as settling or centrifugation. The recovered aqueous hydrogen chloride phase can be recycled to the hydrolysis reactor.

55 The siloxane phase can then be separated into a desired cyclic siloxanes fraction and a chlorosiloxane/hydroxysiloxane fraction by standard means such as flash or column distillation or falling film evaporation. The chlorosiloxanes and hydroxysiloxanes are recycled to the redistribution reactor for redistribution to low molecular weight chlorosiloxanes capable of undergoing hydrolysis to cyclic polysiloxanes. The chlorosiloxanes and hydroxysiloxanes may be recycled

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on a continuous or batch basis. A volume ratio of the second chlorosilane or chlorosiloxane mixture to the recycled chlorosiloxanes and hydroxysiloxanes in the range of 1:1 to 100:1 has been found useful. The preferred ratio will depend upon the molecular weight of the recycled material, the composition of the second mixture and the desired product. A preferred process is where p is zero, R is methyl and the volume ratio of the second mixture to the recycled chlorosiloxanes is in the range of 1:1 to 30:1.

Example 1. (Not within the scope of the instant invention)

A mixture of dimethyldichlorosilane and chloride end-terminated polydimethylsiloxanes, with an average number of siloxane units of 28 per polymer chain, was allowed to react at room temperature for 147 hours. The molar ratio of dimethyldichlorosilane to polydimethylsiloxane was 25:1. The average number of siloxane units per polymer chain of the redistributed mixture was determined by supercritical fluid chromatography (SFC). The sampling times and the results are provided in Table 1.

Table 1

Redistribution of Chloride End-terminated Polysiloxane Polymers In The Absence of Catalyst.	
Time (h)	Polymer Length
0	28.8
5	22.7
51	13.2
99	12.0
147	11.2

The data of Table 1 demonstrate that in the absence of a catalyst the chloride end-terminated polydimethylsiloxanes redistribute slowly.

Example 2

Various materials were tested for their ability to catalyze the redistribution of a mixture of chloride end-terminated polydimethylsiloxanes and dimethyldichlorosilane (DMDCS). The test compounds were soaked overnight in DMDCS, at room temperature, to react away any water present in the catalyst. Chloride end-terminated polydimethylsiloxanes with an average number of siloxane units of approximately 28 were mixed with DMDCS at a molar ratio of 25 moles per mole of siloxane. This mixture of chloride end-terminated polydimethylsiloxanes and DMDCS was then contacted with the pretreated bed of catalyst for eight minutes, at a temperature of 40°C, to effect redistribution. The redistributed mixture was recovered and analyzed by SFC to determine the average molecular weight of the redistributed siloxanes.

Table 2 lists the type materials tested and the source of each material. Tested compounds, as listed in Table 2, were purchase from United Catalyst, Inc., Louisville, KY; Alfa Products, Danvers, MA; Norton, Akron, OH; Calgon, Pittsburgh, PA; and Harshaw, Cleveland, OH.

The percent of linear chloride end-terminated polydimethylsiloxanes in the redistributed mixture less than 6 siloxane units in length is presented under the heading "%Linear<6." The value is calculated as a percent of all linear polydimethylsiloxanes in the redistributed mixture.

Table 2

Screening of Compounds as Catalysts For Redistribution of Chloride End-terminated Polydimethylsiloxanes		
Type Material	%Linears <6	Source
Alumina	96.3	United Catalyst Inc. (CS331-1)
Silica-Alumina (8.4% SiO ₂)	93.3	United Catalyst Inc. (L2271B)
Silica-Alumina (29% SiO ₂)	83.6	United Catalyst Inc. (L2273B)
Y-Zeolite	53.9	Alfa Products
H-Mordenite	4.9	Norton
Erionite	9.9	United Catalyst Inc.
Activated Carbon*	32.0	Calgon (BPL)

* not within the scope of the present invention

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Table 2 (continued)

Screening of Compounds as Catalysts For Redistribution of Chloride End-terminated Polydimethylsiloxanes		
Type Material	%Linears <6	Source
Acid Clay*	18.2	Marshaw Filtral

* not within the scope of the present invention

The data presented in Table 2 demonstrate the ability of various materials to function as catalysts for the redistribution of a mixture of chloride end-terminated polydimethylsiloxanes and dimethylchlorosilanes.

Example 3

A series of runs was conducted to demonstrate that low molecular weight, chloride end-terminated polydimethylsiloxane polymers hydrolyze to cyclic siloxanes.

A continuous stirred-tank reactor (CSTR) was used. The reactor consisted of a 500 ml 3-neck flask equipped with a stirring paddle. The reactor contained a side nozzle from which hydrolysate was continuously removed. The hydrolysate was gravitationally phase separated in a separate vessel to a top siloxane phase and a bottom aqueous hydrogen chloride phase. The aqueous hydrogen chloride phase was recycled to the CSTR. Samples of the siloxane phase were collected for analysis by gas chromatography (GC) and SFC. The required heat for the reaction was provided by heating the recycled aqueous hydrogen chloride prior to returning to the CSTR.

A series of 11 baseline runs was conducted with DMDCS. These runs were conducted at 35°C., with a mixing speed of 600 rpm, a DMDCS feed rate of 12 ml per minute, and with added 42% weight percent aqueous hydrogen chloride.

For comparison, in a second series of runs, monodispersed chloride end-terminated polydimethylsiloxane polymers (CEB_s , where s is the number of silicon atoms) were hydrolyzed. This series of runs was conducted at 35°C., with a mixing speed of 1100 rpm, a CEB_s feed rate of 5 ml per minute, a DMDCS feed rate of 12 ml per minute and with added 42% weight percent aqueous hydrogen chloride. The CEB_s and DMDCS were fed separately into the bottom of the reactor.

The siloxane products from the reactor were analyzed by GC. The percent conversion of feed, DMDCS or CEB_s , to product was calculated using the following formula:

$$\text{%Conv} = \left[\frac{\text{Wt\% Reactants in Feed} - \text{Wt\% Reactants in Product}}{\text{Wt\% Reactants in Feed}} \right] \times 100$$

The normalized percent cyclic yield was calculated from the GC or SFC data using the formula:

$$\text{%Cyclics} = \left[\frac{\text{Wt\% Cyclics}}{\text{ZConv.}} \right] \times 100$$

The percent cyclics of a particular degree of polymerization (%D_s, where s is the number of silicon atoms in the ring) was calculated as:

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$$6 \quad \%D_s = \left[\frac{Wt\%D_s}{Wt\% \text{ Total Cyclics}} \right] \times 100$$

10 The data for these runs is presented in Table 3. The heading "feed" refers to the DMDCS or chloride end-terminated polydimethylsiloxane (CEB_n). The headings % D_s, % Conv, and % Cyclics are as described above.

Table 3

Feed	% Conv	% Cyclics	% D _s			
			D ₃	D ₄	D ₅	D ₆
DMDCS	100	47	1	74	19	4
CEB ₂	100	43	1	72	20	5
CEB ₃	68	43	3	76	17	4
CEB ₄	55	65	0	96	3	1
CEB ₅	71	46	0	22	73	3
CEB ₆	49	12	0	25	21	53

25 The data presented in Table 3 demonstrate that linear chloride end-terminated polydimethylsiloxanes can be hydrolyzed to cyclic species and indicates that the distribution of the cyclics can be influenced by the chain length of the chloride end-terminated polydiorganosiloxane.

30 Example 4

A hydrolysate containing high molecular weight (HMW) chloride end-terminated polydimethylsiloxanes with an average number of about 4000 siloxane units per polymer chain were redistributed with DMDCS. The hydrolysate was mixed with DMDCS at a volume ratio of 0.6:1 and passed through a column of alumina (United Catalysis, CS331-1) held at a temperature of 40°C. The resident time within the alumina bed was about 11.7 minutes. The product from the alumina column was collected and analyzed by SFC for size distribution of the siloxanes. The results are presented in Table 4. The heading "%HMWP" refers to the percent of chloride end-terminated polydimethylsiloxane in the feed or product mixture with an average number of siloxane units of about 4000. The heading "%Linears<6" refers to the percent of chloride end-terminated linears less than six siloxane units in length, as a percent of all linear polydimethylsiloxanes in the product or feed mixture.

Table 4

Redistribution of HMW Chloride End-terminated Polydimethylsiloxanes		
	%HMWP	%Linears<6
Feed	1.2	0.6
Product	<0.1	68.1

50 The data demonstrates the ability of alumina to effect redistribution of HMW chloride end-terminated polydimethylsiloxanes with dimethylidichlorosilane.

55 Example 5

A three-stage process was run. In the first stage of the process, a mixture of chloride end-terminated polydimethylsiloxane polymers and DMDCS was redistributed in a plug-flow reactor. In the second stage of the process, the redistributed siloxane mixture was hydrolyzed in a CSTR reactor similar to that described in Example 3. In the third stage of the process, the hydrolysis mixture of stage 2 was separated into a cyclic siloxane portion and a linear siloxane portion by flash distillation. The linear siloxane portion was recycled back to the first stage of the process for further

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redistribution and conversion to cyclic siloxanes.

In the first stage of the process, a plug-flow reactor, of conventional design, with a packed bed of alumina (United Catalyst, Inc., CS931-1), was used to redistribute chloride end-terminated polydimethylsiloxanes with DMDCS to produce short chain, chloride end-terminated polydimethylsiloxanes. The alumina catalyst was initially soaked with DMDCS to remove water. After removal of residual water, additional DMDCS was continuously metered to the redistribution reactor at a rate of 6.5 to 7.0 ml per minute. Prior to entering the redistribution reactor, the DMDCS was combined with recycled bottom material from the stage 3 flash distillation procedure. The volume ratio of DMDCS to bottom material was maintained within the range of 2:1 to 3:1:1. Residence time of the feed materials within the packed bed of the redistribution reactor was approximately 8 minutes. Samples of the redistributed product were taken and analyzed using SFC.

In the second stage of the process, the short-chain chloride end-terminated polydimethylsiloxanes produced in the redistribution stage were hydrolyzed by continuous feeding to a CSTR similar to that described in Example 3. A co-feed of recycled 42% weight percent aqueous hydrogen chloride was fed to the CSTR along with the redistribution product. A volumetric ratio of approximate 4:1 acid to redistribution product was used. The liquid level in the CSTR was controlled at about 250 ml by withdrawing liquid from a side nozzle. The residence time of feed materials in the CSTR was about 5 minutes. Agitation of the mixture within the CSTR was provided by a stirring paddle rotated at 600 rpm. The CSTR reactor was held at 60°C. by heating the recycled aqueous hydrogen chloride prior to returning to the reactor. The hydrogen chloride gas generated by the reaction was vented at near atmospheric pressure directly to a standard vent scrubber.

The liquid hydrolysis products were continuously taken off the side nozzle of the CSTR and allowed to phase separate in a separate vessel. The bottom phase, consisting of aqueous hydrogen chloride, was recycled to the CSTR. The top phase, containing a mixture of siloxanes, was fed directly to a flash stripper. The interface level in the phase separator was maintained by feeding 36% weight percent aqueous hydrogen chloride to the separator to replenish the water used in the reaction. Samples of the siloxane product were taken and analyzed by GC and SFC.

In the third phase of the process the siloxane mixture, separated from the CSTR process, was fed directly into a 3 liter flash distillation vessel. The distillation vessel was a single-stage flash distillation apparatus operating at a temperature between 230°C. and 250°C. and at near atmospheric pressure. The cyclic siloxanes were distilled off, condensed and collected. The liquid level in the distillation vessel was maintained by adjusting a bottoms take-off pump rate to give a liquid hold up time of approximate 30 minutes. The entire bottoms stream was recycled back to the stage 1 redistribution reactor for chain shortening. Samples of the distillate and the bottom products were taken and analyzed by SFC.

The three-stage process was run continuously over a two day period. The averaged results for samples collected over this time period are presented in Table 4. The data under the heading "%CEB1-5" is a summation of DMDCS and chloride end-terminated polydimethylsiloxane polymers of 1 to 4 siloxane units in length, present in the sample, as a weight percent of the total sample. The headings "%Cyclics" and "%Conv" are as previously described. The heading "%Cyclic Yield" is calculated as:

$$\% \text{Cyclic Yield} = \left[\frac{\text{WT\% Cyclics}}{\% \text{Conv}/100} \right] \times 100$$

The results are presented in Table 5.

Table 5

Results of Three-Stage Process				
Stage	%CEB1-5	%Cyclics	%Conv	%Cyclic Yield
1	96.3	0.7	-	-
2	12.5	41.3	88.9	48.4
3 (overheads) (Bottoms)	16.7 4.9	75.3 22.1	- -	-3 -

The data of Table 5 demonstrate the ability to achieve efficient operation of a three-stage process for producing cyclic siloxanes, where non-volatile cyclics and chloride end-terminated polydimethylsiloxane linear are recycled to

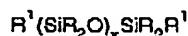
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the process.

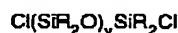
Claims

5 1. A process for the redistribution of chloride or hydroxyl-terminated polyorganosiloxanes, the process comprising:

(A) contacting a first polydispersed mixture comprising siloxanes having the formula

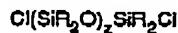


where each R is independently selected from a group consisting of hydrogen, alkyl and substituted alkyl radicals of one to six carbon atoms, R¹ is either Cl or OH, x is a mean value of 1 to 5,000, with a second mixture comprising chlorosilanes or chlorosiloxanes of the formula



20 where R is as previously described and y is a mean value of 0 to less than x in the presence of a catalyst which facilitates redistribution of chlorosiloxanes, the catalyst being selected from a group consisting of alumina, silica alumina, and zeolite for 1 to 60 minutes, and

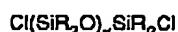
(B) forming a redistributed mixture comprising chlorosiloxanes of the formula



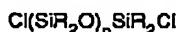
where R is as previously described and z is a mean value greater than y and less than x if R¹ is Cl or less than x + 2y if R¹ is OH.

30 2. A three-stage process for preparing cyclic siloxanes, the process comprising:

(A) contacting a first mixture comprising chlorosiloxanes of the formula

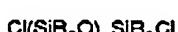


40 where each R is independently selected from a group consisting of hydrogen atoms and alkyl and substituted alkyl radicals of one to six carbon atoms and x is a mean value of one to 5000; with a second mixture comprising chlorosilanes and chlorosiloxanes of the formula



where R is as previously described and p is a mean value of zero to 7; in the presence of a catalyst which facilitates redistribution of chlorosiloxanes selected from a group consisting of alumina, silica alumina, zeolite, and activated carbon;

(B) forming a redistributed mixture comprising chlorosiloxanes of the formula



where R is as previously described and q is a mean value within a range of greater than zero and less than seven;

(C) hydrolyzing the redistributed mixture of chlorosiloxanes to form a hydrolysate comprising cyclic siloxanes of the formula

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where R is as previously described and q is a mean value of three to 25 and chlorosiloxanes;
 5 (D) separating the cyclic siloxanes from the chlorosiloxanes; and
 (E) recycling the chlorosiloxanes as a feed to step (A).

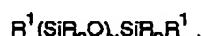
Patentansprüche

10

1. Verfahren zur Umverteilung von Polyorganosiloxanen mit Chlorid- oder Hydroxylendgruppen, wobei das Verfahren umfaßt, daß man:

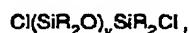
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(A) eine erste polydisperse Mischung aus Siloxanen der Formel



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worin jeder Rest R unabhängig ausgewählt ist aus einer Gruppe bestehend aus Wasserstoff, Alkyl- und substituierten Alkyresten mit 1 bis 6 Kohlenstoffatomen, R¹ entweder Cl oder OH ist, x ein Mittelwert von 1 bis 5.000 ist, mit einer zweiten Mischung aus Chlorsilanen oder Chlorsiloxanen der Formel

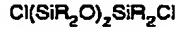


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worin R wie vorher beschrieben ist und y ein Mittelwert von 0 bis weniger als x ist, in Gegenwart eines Katalysators, der die Umverteilung von Chlorsiloxanen erleichtert, 1 bis 60 Minuten lang in Kontakt bringt, wobei der Katalysator ausgewählt ist aus einer Gruppe bestehend aus Aluminiumoxid Siliciumdioxid-Aluminiumoxid und Zeolith, und

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(B) eine umverteilt Mischung aus Chlorsiloxanen der Formel



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bildet, worin R wie vorher beschrieben ist und z ein Mittelwert größer y und kleiner x ist, wenn R¹ Cl ist, oder kleiner x + 2y ist, wenn R¹ OH ist.

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2. Dreistufiges Verfahren zur Herstellung von cyclischen Siloxanen, wobei das Verfahren umfaßt, daß man:

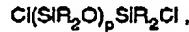
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(A) eine erste Mischung aus Chlorsiloxanen der Formel



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worin jeder Rest R unabhängig ausgewählt ist aus einer Gruppe bestehend aus Wasserstoffatomen und Alkyl- und substituierten Alkyresten mit 1 bis 6 Kohlenstoffatomen, und x ein Mittelwert von 1 bis 5000 ist; mit einer zweiten Mischung aus Chlorsilanen und Chlorsiloxanen der Formel

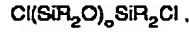


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worin R wie vorher beschrieben ist und p ein Mittelwert von 0 bis 7 ist; in Gegenwart eines Katalysators, der die Umverteilung von Chlorsiloxanen erleichtert, ausgewählt aus einer Gruppe bestehend aus Aluminiumoxid, Siliciumdioxid-Aluminiumoxid, Zeolith und Aktivkohle, in Kontakt bringt;

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(B) eine umverteilt Mischung mit Chlorsiloxanen der Formel



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worin R wie vorher beschrieben ist und o ein Mittelwert in einem Bereich von größer 0 und kleiner 7 ist; bildet; (C) die umverteilte Mischung aus Chlorsiloxanen hydrolysiert unter Bildung eines Hydrolysats, das cyclische Siloxane der Formel

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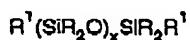
worin R wie vorher beschrieben ist und q ein Mittelwert von 9 bis 25 ist; und Chlorsiloxane umfaßt; (D) die cyclischen Siloxane von den Chlorsiloxanen abtrennt und 10 (E) die Chlorsiloxane als Beschickung in Stufe (A) zurückführt.

Revendications

15 1. Un procédé pour la redistribution de polyorganosiloxanes terminés par des atomes de chlore ou des groupes hydroxyle, le procédé comprenant :

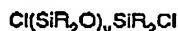
(A) la mise en contact d'un premier mélange polydispersé comprenant des siloxanes répondant à la formule

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où chaque R est choisi de manière indépendante dans l'ensemble formé par l'atome d'hydrogène et les radicaux alkyles et alkyles substitués comptant 1 à 6 atomes de carbone, R¹ est soit Cl soit OH, x a une valeur moyenne de 1 à 5000, avec un deuxième mélange comprenant des chlorosilanes ou des chlorosiloxanes répondant à la formule

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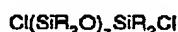


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où R répond à la même définition que précédemment et y a une valeur moyenne de 0 à moins que x, en présence d'un catalyseur qui facilite la redistribution des chlorosiloxanes, le catalyseur étant choisi dans l'ensemble formé par l'alumine, la silice-alumine et une zéolite pendant 1 à 60 minutes, et

(B) à former un mélange redistribué comprenant des chlorosiloxanes répondant à la formule

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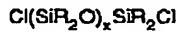
où R répond à la même définition que précédemment et z a une valeur moyenne supérieure à y et inférieure à x si R¹ est Cl ou inférieure à x + 2y si R¹ est OH.

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2. Un procédé en trois temps pour la préparation de siloxanes cycliques, le procédé comprenant les opérations consistant :

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(A) à mettre en contact un premier mélange comprenant des chlorosiloxanes répondant à la formule



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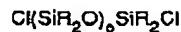
où chaque R est choisi de manière indépendante dans l'ensemble formé par l'atome d'hydrogène et les radicaux alkyles et alkyles substitués comptant 1 à 6 atomes de carbone et x a une valeur moyenne de 1 à 5000, avec un deuxième mélange comprenant des chlorosilanes et des chlorosiloxanes répondant à la formule



où R répond à la même définition que précédemment et y a une valeur moyenne de 0 à 7, en présence d'un catalyseur facilitant la redistribution des chlorosiloxanes choisi dans l'ensemble formé par l'alumine, la silice-

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alumine, une zéolite et un charbon actif ;
(B) à former un mélange redistribué comprenant des chlorosiloxanes répondant à la formule



où R répond à la même définition que précédemment et α a une valeur moyenne supérieure à 0 et inférieure à 7 ;

10 (C) à hydrolyser le mélange de chlorosiloxanes redistribué pour former un hydrolysat comprenant des siloxanes cycliques répondant à la formule



15 où R répond à la même définition que précédemment et q a une valeur moyenne de 3 à 25 et des chlorosiloxanes ;

(D) à séparer les siloxanes cycliques des chlorosiloxanes ; et
(E) à recycler les chlorosiloxanes comme matières premières pour l'opération (A).

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